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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Process for the Treatment of Vinyl Chloride Polymers

We, FARBENFABRIKEN BAYER AKTIEN-
GESELLSCHAFT, a body corporate organised
under the laws of Germany, of Leverkusen-
Bayerwerk, Germany, do hereby declare the
invention, for which we pray that a patent
may be granted to us, and the method by
which it is to be performed, to be particu-
larly described in and by the following state-
ment:

10 The present invention is concerned with
a process for treating vinyl chloride poly-
mers.

According to the present invention, there
is provided a process which consists in that
15 vinyl chloride polymers are mixed with co-
polymers from ethylene and vinyl esters and
with radical-forming substances and then
heated at temperatures of 50 to 200°C dur-
ing or after moulding.

20 The term vinyl chloride polymers also
comprises, in the present case, copolymers
of vinyl chloride with other vinyl com-
pounds, for example, with vinyl esters, such
as vinyl acetate, or also with vinylidene
25 chloride. The polymers can be produced in
any way, for example, by the emulsion or
suspension method; the degree of their poly-
merisation may lie within a wide range, poly-
mers with K-values of 50 to 80 having
30 proved to be especially advantageous.

The vinyl chloride polymers should ex-
pediently contain plasticisers, for example
esters of phthalic acid, such as diethyl
phthalate, dibutyl phthalate or dinonyl
35 phthalate, esters of phosphoric acid, such as
tricresyl phosphate, or esters of sebacic acid
and adipic acid, such as dioctyl sebacate and
dibutyl adipate. Depending upon the in-
tended purpose of processing or use, the
40 vinyl chloride polymers may also contain

further additives, such as stabilisers, lubri-
cants, fillers, wood powder and glass fibers,
as well as dyestuffs and pigments. An addi-
tion of basic substances, especially metal
oxides, such as magnesium oxide, has also
proved useful in many cases.

Examples of copolymers of ethylene and
vinyl esters are the copolymers of ethylene
with vinyl acetate, vinyl propionate, vinyl
stearate and/or vinyl benzoate. They can be
produced by any desired method, for ex-
ample, according to the process of British
Patent Specification No. 843,974. The pro-
portion of ethylene to vinyl esters may vary
within wide limits, for example between 20
50 to 80 parts of ethylene, on the one hand,
and 80 to 20 parts of vinyl esters, on the
other hand.

Suitable mixing proportions between the
vinyl chloride polymers and the ethylene/
vinyl ester copolymers can easily be ascer-
tained by preliminary experiments. In
general, it is advisable to use 5 to 50 parts
by weight of ethylene/vinyl ester copolymer
per 100 parts by weight of vinyl chloride
polymer.

Examples of radical-forming substances are
the esters of azo-dicarboxylic acid, further-
more peroxides, such as benzoyl peroxide, di-
chlorobenzoyl peroxide, *tert.*-butyl hydroper-
oxide, di-*tert.*-butyl peroxide, peroxy-dicar-
bonates, polymeric phthalyl peroxide, adipic
acid - bis - *tert.* - butylperester, 2,5 - bis -
(*tert.*- butylperoxy) - 2,5 - dimethyl - hexane
or dicumyl peroxide. They are generally
used in an amount of 0.2 to 10 parts by
weight, referred to 100 parts by weight of
ethylene/vinyl ester copolymer.

In many cases, it is expedient to add to
the mixtures of vinyl chloride polymers,

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ethylene/vinyl ester copolymers and radical-forming substances and also minor amounts of monomeric polymerisable compounds containing two or more olefinic double bonds, 5 for example, triallyl cyanurate or triallyl phosphate, preferably in amounts of 0.5 to 10 parts by weight, referred to 100 parts by weight of ethylene/vinyl ester copolymer.

In order to mix the components concerned, 10 the devices customary in industry can be used, for example kneaders or mixing rolls.

The time and temperature required for heating the mixtures depend upon the thermal stability and the rate of decomposition 15 of the radical-forming substances. In general, the temperature lies between 50 and 200°C. with a heating period of between 60 minutes and 5 seconds.

The vinyl chloride polymers treated 20 according to the process of the present invention offer a number of advantages over untreated vinyl chloride polymers. They do not become sticky when heated and do not stick to hot surfaces; mouldings produced 25 from the treated vinyl chloride polymers can, therefore, be removed from the mould after shaping while hot, whereas mouldings from untreated vinyl chloride polymers necessitate cooling of the moulds before removal of the polymers. Furthermore, the 30 vinyl chloride polymers treated by the process according to the present invention are no longer plastic at elevated temperatures, but elastic; furthermore, they exhibit an 35 improved stability to organic solvents. The process of the present invention can, therefore, be used with advantage for the production of tubes, profiles or cable sheathings.

40 The process according to the present invention, it is of special importance for the production of coatings, for example, on textiles, fleeces, paper, leather, artificial leather, wood and metals. The procedure for this 45 purpose may be such that the mixtures concerned are applied in the form of solutions, dispersions or foils to the substrates possibly provided with adhesives, followed, after removal of the solvent or dispersing agent, 50 by heating, expediently with compression shaping.

The following Examples are given for the purpose of illustrating the present invention, the parts given being parts by weight:—

EXAMPLE 1:

100 parts polyvinyl chloride (produced by the suspension method: K-value 65) 20 parts ethylene/vinyl acetate copolymer (produced from 52 parts of ethylene and 48 parts of 55 vinyl acetate: Mooney plasticity ML4¹-100°C:25), 100 parts dioctyl phthalate, 1 part basic lead sulphate, and 10 parts magnesium oxide are mixed with one another on mixing rolls at 160°C, for 5 minutes. To the homo-

geneous mixture, there are subsequently added 65 on a roller, heated to about 40°C., 1 part stearic acid, 25 parts highly-active, precipitated silicic acid, 3 parts iron oxide, 3 parts dibenzoyl peroxide, and 3 parts triallyl cyanurate.

The mixture thus obtained is then stretched 70 to a foil, the foil is applied to chrome-tanned skivers and heated at 120°C. in a press under a pressure of 2 kg/cm² for 10 Minutes. The coating thus formed can be released 75 while hot; it is no longer thermoplastic.

EXAMPLE 2:

100 parts of a polymer with K-value 55, prepared from 85 parts vinyl chloride and 15 parts vinyl acetate by the emulsion method, 80 40 parts ethylene/vinyl acetate copolymer (prepared from 30 parts ethylene and 70 parts vinyl acetate; Mooney plasticity ML4¹-100°C:15); 50 parts dioctyl phthalate, 1 part basic lead sulphate and 10 parts magnesium oxide are mixed with one another in an internal mixer at 160°C. for 5 minutes. To the homogeneous mixture there are subsequently added on a roller, heated to about 60°C. 1 part stearic acid, 20 parts highly-active silicic acid, 2 parts dicumyl peroxide and 3 parts triallyl cyanurate.

The mixture thus obtained is then injection-moulded and heated at 150°C. for 15 minutes in a compression mould under a pressure of 5 kg/cm². The profile thus obtained can be removed from the mould while hot; it shows a very good resilience under compressive stress at room temperature, as well as at 70°C.

EXAMPLE 3:

100 parts of a polymer of K-value 50, prepared from 80 parts of vinyl chloride and 20 parts of vinylidene chloride by the emulsion method, 20 parts of an ethylene/vinyl propionate copolymer (prepared from 65 parts of ethylene and 35 parts of vinyl propionate; Mooney plasticity ML4¹-100°C:25) 105 100 parts of an ester from phenol and a paraffin-sulphonic acid chloride containing about 15 carbon atoms, 2 parts basic lead carbonate and 25 parts magnesium oxide are mixed with one another on mixing rolls at 160°C. for 5 minutes. To the homogeneous mixture, there are subsequently added on a roller, heated to about 40°C., 1 part stearic acid, 25 parts precipitated silicic acid, 3 parts 110 2,5 - bis - (tert. - butylperoxy) - 2,4 - di - methyl-hexane, and 3 parts triallyl phosphate. The mixture thus obtained is then stretched to a foil, placed on a cotton fabric and heated at 150°C. for 15 minutes in a press under a pressure of 3 kg/cm². A non-thermoplastic leather cloth is thus obtained which 115 can be removed while hot.

WHAT WE CLAIM IS:—
1. A process for the treatment of vinyl

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- chloride polymers and copolymers, which consists in that vinyl chloride polymers or copolymers are mixed with copolymers from ethylene and vinyl esters and with radical-forming substances, and then heated at temperatures of 50 to 200°C. during or after moulding.
2. A process according to claim 1, wherein the vinyl chloride polymers or copolymers used have a k-value of 50 to 80.
3. A process according to Claim 1 or 2, wherein 5 to 50 parts by weight of ethylene-vinyl ester copolymer are used for 100 parts by weight of vinyl chloride polymer or copolymer.
4. A process according to any of the preceding claims, wherein 0.2 to 10 parts by weight of radical forming substances are used for 100 parts by weight of ethylene-vinyl ester copolymer.
5. A process according to any of the preceding claims, wherein there is additionally used a minor amount of monomeric polymerisable compounds containing two or more olefinic double bonds.
6. A process according to claim 5, where-
- in the additional polymerisable compound is used in an amount of 0.5 to 10 parts by weight per 100 parts by weight of ethylene-vinyl ester copolymer.
7. A process according to any of the preceding claims, wherein the treatment is carried out for a period of 60 minutes to 5 seconds at a temperature between 50 and 200°C.
8. A process according to claim 1 for the treatment of vinyl chloride polymers and copolymers, substantially as hereinbefore described and with reference to any of the specific Examples.
9. Vinyl chloride polymers and copolymers, whenever treated by the process according to any of claims 1 to 8.
10. Coatings and moulded articles, whenever prepared from a vinyl chloride polymer or copolymer according to claim 9.

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